

# **FORWARD OSMOSIS FOR WASTEWATER RECLAMATION: TRACE ORGANIC CONTAMINANTS REMOVAL AND COOLING FOR POST-COMBUSTION CO<sub>2</sub> CAPTURE**

**By Lei Zheng**

Thesis submitted in fulfilment of the requirements for  
the degree of

**Doctor of Philosophy**

under the supervision of Long D. Nghiem, Qilin Wang and  
William E. Price

University of Technology Sydney  
Faculty of Engineering and Information Technology

June 2020

***This thesis is dedicated to my parents***

***Liyang Liu and Xiaohong Zheng***

***For their endless love, support and encouragement***

## **Certificate of Original Authorship**

I, **Lei Zheng** declare that this thesis, is submitted in fulfilment of the requirements of the award of **Doctor of Philosophy**, in the School of Civil and Environmental Engineering at the University of Technology Sydney.

I also certify that the work in this thesis has not previously been submitted for a degree nor it has been submitted as part of requirements for a degree except as fully acknowledged within the text.

This thesis is wholly my own work unless otherwise reference or acknowledged. Any help that I have received in my research and preparation of the thesis has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. This research is supported by the Australian Government Research Training Program.

Signature of Student: Lei Zheng

Date: June 17<sup>th</sup>, 2020

Production Note:  
Signature removed  
prior to publication.

## Acknowledgements

First and foremost, I would like to express my sincere gratitude and appreciation to my Principal Supervisor Professor Long Nghiem for his guidance and support of my PhD study. His enthusiasm for research and life has inspired me to achieve the great goals during last four years. In addition, his patience, encouragement and immense knowledge boost my confidence to conquer the challenges in all the time of my research and thesis writing. Furthermore, his detail-oriented attitude teaches me how to be a qualified scientist in future. I am so fortunate to be one of his students and share this amazing journey with him.

Besides, I would like to thank my Co-Supervisor Dr Qilin Wang, External Supervisor Professor William Price, co-authors, reviewers and teachers for their invaluable comments and encouragement in my research work, which greatly incited me to gain thorough insights and widen my knowledge for membrane technology.

My appreciation also extends to my colleagues, whose support and encouragement have helped me overcome the dilemma in the past. They are Ashley, Richard, Minh, Bilal, Allie, Luong, Wenhai, Hung, Sherry, Aileen, Lewa, Jameshed, Hop, Sultan, Tabea, Sihuang, and Biplob. I will never forget the moment when we raised Uniclub Cup Championship Trophy from our great teamwork. Special thanks to the technician staffs: Linda, Johir, and Nirenkumar for their kind assistances in my experimental work.

I sincerely cherish the visiting opportunity offered by Kangkang in CSIRO Energy Centre, Newcastle. His expertise in CO<sub>2</sub> capture technology motivated me to combine membrane process with CO<sub>2</sub> capture.

I would like to thank Samantha for her tremendous guidance in presentation skills and support in entrepreneurship. She is a warm-hearted person who always encourages me towards the vision of bright future.

Apart from PhD study, I volunteered to be an international student mentor that offered me a great chance to assist other international students to grow independence abroad and impart my professional knowledge in the cross-cultural communication. I greatly appreciate the opportunity provided by Ms Liju Dong.

Studying abroad is not always easy since you have to constantly adapt to a new environment. I feel extremely lucky to meet a group of the amazing people, who have greatly helped me overcome obstacles and enjoyed the happiness together during this period. They are Luisa, Joana, Azita, Douglas, Lin, Chunyang, Long, Guanyu, Le, Jiantao, Lan, Qiang, Shiyu, Emily, Jiawei, Minwei, Zhijie, Hanjie, Huan, Chen, Xiaoqing, Dongle, Bing, Bentuo, Zehao, Phong, and Haoding. I thank them for bringing lots of beautiful memories in my life.

Family is the greatest source for me to provide the consistent inspiration. I would like to thank my families, their love and affection assist me to pursue my dream. Special thanks to my parents and grandma for always showing their positive attitude towards challenges in life. My sincere appreciation goes to Weilin and her family for their support and caring in the past 6 years. The generous caring from my landlords Milka and Frank make me feel never alone in this country. Frank passed away due to ill health during my study. I wish him could see my achievement today and may his soul rest in peace.

Last but not least, I greatly acknowledge the scholarship support from Chinese Scholarship Council, University of Technology Sydney, and University of Wollongong.

## Research Outcome Summary

### Refereed Journal Papers

- 1) **L. Zheng**, W.E. Price, T. He, and L.D. Nghiem, Simultaneous cooling and provision of make-up water by forward osmosis for post-combustion CO<sub>2</sub> capture. *Desalination*, 476 (2020), 1-7.
- 2) **L. Zheng**, W.E. Price, J. McDonald, S.J. Khan, T. Fujioka, and L.D. Nghiem, New insights into the relationship between draw solution chemistry and trace organic rejection by forward osmosis. *Journal of Membrane Science*, 587 (2019), 1-10.
- 3) **L. Zheng**, W.E. Price, and L.D. Nghiem, Effects of fouling on separation by forward osmosis: the role of specific organic foulants. *Environmental Science and Pollution Research*, 26 (2018), 33758-33769.

### Submitted and In-preparation Journal Papers

- 1) **L. Zheng**, K.K. Li, Q.L. Wang, G. Naidu, W.E. Price, X.W. Zhang, and L.D. Nghiem, Low-temperature stripping of CO<sub>2</sub> from aqueous amine-based solvents via integrated direct contact membrane distillation-forward osmosis, *Journal of Membrane Science*, Submitted.
- 2) M. Krajewska, **L. Zheng**, M. Szczygiel, L.D. Nghiem, and K. Prochaska, Bio-carboxylic acid recovery from fermentation broth by integrated forward osmosis -reverse osmosis system, *Journal of Membrane Science*, in preparation.

### Conference Presentation

- 1) **L. Zheng** and L.D. Nghiem, Regeneration of amine-based solvent via integrated direct contact membrane distillation - forward osmosis (DCMD-FO) for post-combustion CO<sub>2</sub> capture. Oral presentation at the *10<sup>th</sup> International Membrane Science & Technology Conference*, Sydney, 2<sup>nd</sup> - 6<sup>th</sup> February 2020.
- 2) **L. Zheng** and L.D. Nghiem, New insights into the relationship between draw solution chemistry and trace organic rejection by forward osmosis. Oral presentation at the *2<sup>nd</sup> Green Technologies for Sustainable Water*, Ho Chi Minh City, 1<sup>st</sup> - 5<sup>th</sup> December 2019.

- 3) **L. Zheng** and L.D. Nghiem, Simultaneous cooling and provision of make-up water by forward osmosis for post-combustion CO<sub>2</sub> capture. Oral presentation at the *2<sup>nd</sup> International Conference on Energy-Efficient Separation*, Melbourne, 27<sup>th</sup> - 30<sup>th</sup> December 2019.
- 4) **L. Zheng** and L.D. Nghiem, Effects of fouling on separation by forward osmosis: the role of specific organic foulants. Oral presentation at the *6<sup>th</sup> Membrane of Australasia Early Career Researcher Membrane Symposium*, Melbourne, 30<sup>th</sup> - 1<sup>st</sup> February 2019.
- 5) **L. Zheng** and L.D. Nghiem, Effects of fouling and chemical cleaning on the rejection of trace organic contaminants by forward osmosis. Oral presentation at the *9<sup>th</sup> International Conference in Challenges in Environmental Science & Engineering*, Kaohsiung, 6<sup>th</sup> - 10<sup>th</sup> November 2016.

### **Awards and Prizes**

- 1) First Prize in Three Minutes Short Talk – Best Overall Award at the *2<sup>nd</sup> International Conference on Energy-Efficient Separation*, 2019, Melbourne.
- 2) People’s Choice Award for Oral Presentation at the *Civil and Environmental Engineering School Research Showcase*, 2019, University of Technology Sydney.
- 3) People’s Choice Award for Oral Presentation at the *Three Minutes Thesis Competition in Faculty of Engineering and Information Technology*, 2019, University of Technology Sydney.
- 4) Winner of Travel Award, one of 15 student representatives for the research exchange program in Poznan University of Technology, 2019, Poznan.
- 5) Winner of Travel Award, *6<sup>th</sup> Membrane Society of Australasia Early Career Researcher Symposium*, 2019, Melbourne.
- 6) A Prize for Excellence at the *12<sup>th</sup> Chunhui Chinese Students Innovations and Entrepreneurship Competition*, 2017, Guangzhou.
- 7) A Prize for Excellence at the *3<sup>rd</sup> Western China Overseas Hi-tech and High Talents Entrepreneurship Competition (Oceania Division)*, 2017, Sydney.

# Table of Contents

Certificate of Original Authorship .....	II
Acknowledgements .....	III
Research Outcome Summary .....	V
Table of Contents .....	VII
List of Figures .....	XI
List of Tables.....	XIII
List of Abbreviations.....	XIV
Abstract .....	XV
<b>Chapter 1 Introduction</b> .....	<b>1</b>
1.1 Background .....	1
1.2 Objectives .....	3
1.3 Research Questions .....	3
1.4 Organization .....	3
<b>Chapter 2 Literature Review</b> .....	<b>6</b>
2.1 Introduction .....	6
2.2 Transport phenomena in FO .....	7
2.2.1 Water permeation and solute transport .....	7
2.2.2 External concentration polarisation.....	8
2.2.3 Internal concentration polarisation.....	9
2.3 Types of membrane fouling in FO .....	9
2.3.1 Organic fouling .....	11
2.3.2 Colloidal fouling .....	12
2.3.3 Scaling.....	13
2.3.4 Biofouling .....	15
2.4 Removal of TrOCs by FO .....	17
2.4.1 Threats from TrOCs .....	17
2.4.2 Impact of membrane fouling on TrOCs removal in FO.....	18
2.4.3 Impact of draw solution chemistry on TrOCs removal in FO .....	21
2.5 Innovative FO application in post-combustion CO <sub>2</sub> capture.....	23
2.5.1 Water usage in amine-based solvent absorption .....	23



2.5.2 Make-up water production by FO .....	25
2.6 Conclusion.....	26
<b>Chapter 3 Effects of fouling on separation performance by forward osmosis: the role of specific organic foulants .....</b>	<b>27</b>
3.1 Introduction .....	27
3.2 Materials and Methods .....	28
3.2.1 Materials.....	28
3.3 Experimental systems.....	29
3.4 Membrane characterisation .....	30
3.4.1 Membrane active layer transport properties.....	30
3.4.2 Membrane support layer structural properties .....	31
3.4.3 Determination of the membrane average pore radius .....	31
3.4.4 Membrane surface charge and hydrophobicity .....	33
3.5 Forward osmosis experiments .....	34
3.6 Analytical methods.....	35
3.7 Results and discussion.....	36
3.7.1 Membrane transport parameters.....	36
3.7.2 Membrane average pore radius .....	37
3.7.3 Organic characterization of model organic foulants by LC-OCD .....	37
3.7.4 Impact of fouling on membrane surface charge and hydrophobicity .....	39
3.7.5 Impact of fouling on water and reverse salt flux.....	41
3.7.6 Impact of fouling on the removal of TrOCs.....	44
3.8 Conclusion.....	46
<b>Chapter 4 New insights into the relationship between draw solution chemistry and trace organic rejection by forward osmosis.....</b>	<b>48</b>
4.1 Introduction .....	48
4.2 Material and Methods.....	49
4.2.1 Materials and trace organic contaminants.....	49
4.2.2 Experimental system and protocol .....	50
4.3 Analytical methods.....	52
4.3.1 Membrane morphology analysis .....	52
4.3.2 Municipal sewage characterization .....	52
4.3.3 Trace organic contaminant analysis .....	52
4.4 Results and discussion.....	53
4.4.1 Impact of draw solution chemistry on water flux and reverse salt flux.....	53

4.4.1 Reverse salt flux selectivity .....	58
4.4.2 Rejection of TrOCs by FO .....	59
4.4.1 Rejection of TrOCs with the presence of fouling .....	63
4.5 Conclusions .....	66
<b>Chapter 5 Simultaneous cooling and provision of make-up water by forward osmosis for post-combustion CO<sub>2</sub> capture.....</b>	<b>67</b>
5.1 Introduction .....	67
5.2 Material and Methods.....	68
5.2.1 FO membrane.....	68
5.2.2 Feed solution .....	69
5.2.3 Draw solution.....	69
5.2.4 Analysis.....	70
5.2.5 Experiment system.....	70
5.2.6 Experiment protocol.....	71
5.3 Results and discussion.....	72
5.3.1 Properties of amine-based CO <sub>2</sub> adsorbents .....	72
5.3.2 Amine-based CO <sub>2</sub> adsorbent as draw solute .....	75
5.3.3 Reverse diffusion of amine-based CO <sub>2</sub> adsorbent .....	77
5.3.4 Effects of operating conditions on water flux .....	79
5.4 Conclusions .....	82
<b>Chapter 6 Low-temperature stripping of CO<sub>2</sub> from aqueous amine-based solvents via integrated direct contact membrane distillation-forward osmosis .....</b>	<b>83</b>
6.1 Introduction .....	83
6.2 Materials and methods.....	86
6.2.1 Membranes and chemicals .....	86
6.2.2 Feed solution for DCMD and FO .....	87
6.2.3 DCMD for CO <sub>2</sub> desorption and FO for water supplement .....	87
6.2.4 Measurement and analysis .....	89
6.3 Results and discussions .....	91
6.3.1 DCMD performance for CO <sub>2</sub> desorption .....	91
6.3.2 Make-up water production in FO performance.....	97
6.3.3 Repetitive CO <sub>2</sub> absorption from regenerated solvents.....	99
6.4 Future work for practical applications.....	99
6.5 Conclusion.....	100
<b>Chapter 7 Conclusions and recommendations for future work .....</b>	<b>101</b>

7.1	Conclusions .....	101
7.2	Recommendations for future work.....	103
	Appendix - Supplementary Data.....	105
	Reference.....	113

## List of Figures

Figure 1-1. Thesis outline .....	5
Figure 2-1: A diagram of water permeation in (a) FO and (b) RO .....	7
Figure 2-2: Direction and magnitude of water flux as a function of applied .....	8
Figure 2-3: Concentration profile across the membrane because of ICP. ....	9
Figure 2-4: Four types of fouling during the membrane treatment (adapted from .....	10
Figure 2-5: Scanning Electron Microscope (SEM) images of organic. ....	12
Figure 2-6: SEM images of FO membrane surface fouled with: (a).....	13
Figure 2-7: SEM images of scaling on different location of FO. ....	14
Figure 2-8. Schematic description of the proposed mechanisms. ....	15
Figure 2-9: Different hypothesis about rejection of TrOCs by. ....	20
Figure 2-10. A schematic diagram of chemical absorption process .....	25
Figure 2-11: Replacement of the trim cooler by forward osmosis.....	26
Figure 3-1: The schematic diagram of the forward osmosis system.....	30
Figure 3-2: LC-OCD chromatograms of sodium alginate (SA) and.....	38
Figure 3-3: Zeta potential of the active layer of membrane samples.....	40
Figure 3-4: Water flux of the membrane at the presence of different.....	43
Figure 3-5: The reverse salt flux of the membrane at the presence of.....	44
Figure 3-6: Sulfamethoxazole rejection by the clean and fouled membrane.....	46
Figure 3-7: Carbamazepine rejection by the clean and fouled membrane.....	46
Figure 4-1: Schematic diagram of the bench-scale forward osmosis system. ....	50
Figure 4-2: Water flux as a function of time. In (a) – (c), DI water .....	54
Figure 4-3: Reverse salt flux and pH in the feed solution.....	55
Figure 4-4: Comparison of reverse salt flux resulted from. ....	56
Figure 4-5: A schematic diagram of coupled effects resulting. ....	57
Figure 4-6: Average water flux, RSF and RSFS of two. ....	58
Figure 4-7: TrOC rejection at buffered pH 6.7. Experimental.....	60
Figure 4-8: Rejection of ionisable TrOCs at different buffered pH.....	61
Figure 4-9: Impact of draw solution species on TrOCs rejection. ....	62
Figure 4-10: Impact of fouling on the water flux: DI water or. ....	63
Figure 4-11: LC-OCD chromatograms of (a) feed, (b) permeate. ....	64

Figure 4-12: TrOCs rejection by clean and fouled membranes. ....	65
Figure 5-1: A bench-scale forward osmosis system .....	71
Figure 5-2: Electrical conductivities of the draw solution as a function of . ....	73
Figure 5-3: Osmotic pressures of NaCl, glycine and MEA solutions as a .....	74
Figure 5-4: Water flux profile as a function of time using different draw.....	75
Figure 5-5: Reverse salt fluxes and specific reverse salt fluxes of. ....	77
Figure 5-6: FO performance in two membrane orientations. (a) .....	80
Figure 5-7: Comparison in water flux when using seawater or .....	81
Figure 6-1: Schematic diagram of integrated DCMD-FO system for CO <sub>2</sub> capture.....	86
Figure 6-2. Schematic diagram of experimental apparatus for CO <sub>2</sub> desorption .....	88
Figure 6-3: CO <sub>2</sub> desorption of CO <sub>2</sub> rich-loaded solvent by using DCMD. ....	92
Figure 6-4: Contact angles of membranes before and after DCMD process. ....	94
Figure 6-5: Water flux in DCMD during CO <sub>2</sub> desorption using.....	95
Figure 6-6: Infrared spectra of the aqueous 30 wt % MEA (black line),.....	97
Figure 6-7: Water flux profile for regenerated solvents versus DI water .....	98

## **List of Tables**

Table 2-1 Characteristics of each membrane fouling .....	10
Table 2-2: Effect of draw solution chemistry on FO performance. ....	21
Table 3-1: Key physicochemical properties of sulfamethoxazole and carbamazepine. .	29
Table 3-2: Comparison of key transport parameters between the TFC .....	36
Table 3-3: Estimated average membrane pore radii of the clean.....	37
Table 3-4 Calculated average membrane pore radii of the CTA. ....	37
Table 3-5 Comparison of the contact angle of membrane layers.....	41
Table 4-1: Characteristics of primary treated municipal sewage.....	49
Table 5-1: Key physicochemical properties of draw solutions.....	69
Table 6-1: Specifications of hydrophobic membranes used in this study.....	87
Table 6-2: CO <sub>2</sub> loading $\alpha$ from selected solvents in the different stage.....	99

## List of Abbreviations

Abbreviation	Meaning
AL-DS	Active Layer Facing Draw Solution
AL-FS	Active Layer Facing Feed Solution
BEOP	Biofilm-Enhanced Osmotic Pressure
CA	Cellulose Acetate
CEOP	Cake-Enhanced Osmotic Pressure
COD	Chemical Oxygen Demand
CTA	Cellulose Triacetate
DCMD	Direct Contact Membrane Distillation
DF	Dilution Factor
DI water	Deionized Water
DOC	Dissolved Organic Carbon
DS	Draw Solution
ECP	External Concentration Polarisation
EDX	Energy Dispersive X-ray Spectroscopy
FO	Forward Osmosis
FS	Feed Solution
FTIR	Fourier Transform Infrared Spectroscopy
HA	Humic Acid
HOAc	Acetic acid
ICP	Internal Concentration Polarisation
LC-OCD	Liquid Chromatography with Organic Carbon Detection
LiCl	Lithium Chloride
LMW	Low Molecular Weight
MD	Membrane Distillation
MEA	Monoethanolamine
MPA	Minimum Projection Area
MW	Municipal Wastewater
NaH <sub>2</sub> PO <sub>4</sub>	Sodium Dihydrogen Phosphate
NaOAc	Sodium Acetate
NF	Nanofiltration
RO	Reverse Osmosis
RSF	Reverse Salt Flux
RSFS	Reverse Salt Flux Selectivity
SA	Sodium Alginate
SG	Sodium Glycinate
SRSF	Specific Reverse Salt Flux
TFC	Thin Film Composite
TOC	Total Organic Carbon
TrOCs	Trace Organic Contaminants
TSS	Total Suspended Solids

## Abstract

Water scarcity and global warming are two vexing and intertwined problems with significant impacts on human society and eco-system. Forward osmosis (FO) can potentially be used as an effective tool for wastewater reclamation and alleviating global warming. This study aimed to explore new approaches to deploy FO toward these objectives. This study elucidated the rejection mechanisms of 43 trace organic contaminants (TrOCs) by FO through a systematic investigation of several influencing factors including draw solution chemistry, contaminants species and membrane fouling. This study also demonstrated the viability of FO as an alternative trim cooler in post-combustion CO<sub>2</sub> capture and repetitive CO<sub>2</sub> capture via direct contact membrane distillation - forward osmosis (DCMD-FO) system.

Results from this study revealed that membrane fouling could induce considerable effects on TrOCs rejection via investigations of three specific organic foulants. Municipal wastewater resulted in a more compact fouling cake layer than that caused by humic acid and sodium alginate, which was likely due to large constituents of low molecular weight neutrals and acids. In addition, fouling altered the membrane less negatively charged and less hydrophilic. Steric hindrance caused by the additional filtration cake layer therefore became the dominant rejection mechanism for sulfamethoxazole. However, lower rejection of carbamazepine was likely due to the cake-enhanced concentration polarization.

Through a systemic investigation, results from this study heightened the inherent complexity in TrOCs rejection by FO. Due to the intrinsic bidirectional transport phenomenon, the reverse flux of proton (or hydroxyl radical) could alter the feed solution pH, which governed the separation of ionizable TrOCs. In addition, variation in hydrated radius of draw solution resulted in the sharp contrast in terms of reverse salt flux (NaCl: 33 g/m<sup>2</sup>h; LiCl: 2 g/m<sup>2</sup>h) and therefore different ionic strength of feed, thus the corresponding electrostatic interaction. Charged compounds generally exhibited higher rejections than neutral ones by the clean membrane, which indicated that electrostatic interaction rather than steric hindrance was the dominant rejection mechanism.



Intrinsic osmotic driving force also enlightened this study to apply FO as an alternative to a trim cooler in post-combustion CO<sub>2</sub> capture. Regenerated amine-based solvents, such as glycine, sodium glycinate, and monoethanolamine (MEA) were successfully used as the draw solution to extract water from treated effluent or seawater, which could provide the make-up water for CO<sub>2</sub> capture. Glycine showed a higher water flux, a lower reverse salt flux and specific reverse salt flux than sodium glycinate and MEA in both membrane orientations, thus was selected for further investigations.

A higher water flux but with considerable flux decline were observed when active layer faced draw solution. Temperature increase in draw solution could alter thermodynamics properties of glycine, thus, resulting in an increase of reverse salt flux. It enhanced water flux due to the diminishing concentrative internal concentration polarisation. On the other hand, changes in water flux were insignificant when active layer faced feed solution even as temperature increased. It appears that temperature increase was likely to aggravate the severity of dilutive internal concentration polarisation and offset the growth of osmotic pressure. Despite of the lower water transportation from seawater than treated effluent due to the less osmotic gradient, seawater could also be as an alternative cooling source and desalinated simultaneously.

This study also demonstrated 85 and 89% of re-absorption capacities for MEA and sodium glycinate in a hybrid DCMD-FO system respectively via the low regeneration temperature. The DCMD achieved respective 33.6 and 33.2% of desorption efficiency for MEA and sodium glycinate at 80 °C. Unlike negligible change caused by sodium glycinate, MEA resulted in either increase or decrease of hydrophobicity for each MD membrane, thus a partial wetting as well. Water production declines were observed for both solvents due to the membrane wetting. However, the high solvent rejection indicated that DCMD resulted in the negligible amine loss.

Regenerated MEA and sodium glycinate resulted in the contrast water flux when deionised water was used as the feed (MEA: 27 L/m<sup>2</sup>h, Sodium glycinate: 14 L/m<sup>2</sup>h). They both whereas showed a similar water flux (15 L/m<sup>2</sup>h) when treated effluent was used as the feed. In addition, sodium glycinate presented a smaller reverse salt flux than that of MEA for both deionised water and treated effluent. A particular membrane structure may lead to the disparity in water flux. More research work is required for the cost-effective CO<sub>2</sub> capture based on membrane system.